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VALENCE PHOTOISOMERIZATION OF 1-ETHOXCARBONYL-1H-AZEPINE:
EXCITED STATE ENERGETICS AND MULTIPLICITY

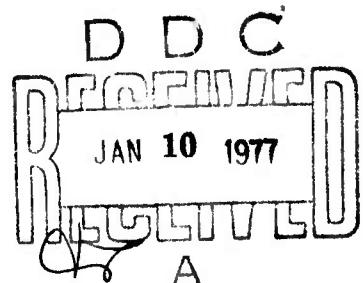
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VALENCE PHOTOISOMERIZATION OF 1-ETHOXCARBONYL-1H-AZEPINE.

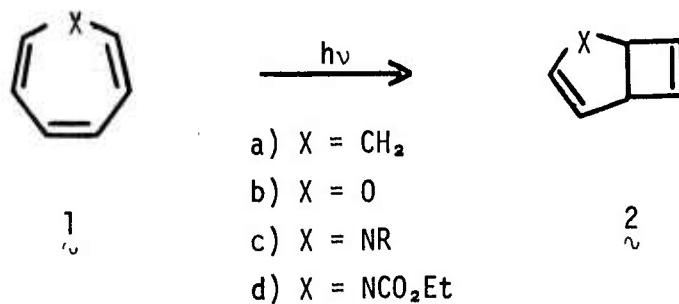
EXCITED STATE ENERGETICS AND MULTIPLICITY.

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The general importance of photochemical valence isomerization $\text{1} \rightarrow \text{2}$ for systems related to 1,3,5-cycloheptatriene is well recognized.¹ Quantitative studies directed to the identification of excited states responsible for isomerization and the general location of states for the cyclic trienes are rare. We supply here such detail concerning the previously reported^{1d} isomerization $\text{1d} \rightarrow \text{2d}$. The absorption, photosensitization and quenching data fortuitously combine to provide quantitative information which is normally unavailable in the absence of triene luminescence.



Irradiation of $\tilde{1d}$ in the region of n, II^* absorption² gave $\tilde{2d}$ in high yield.

Quantum yields for isomerization in solution with and without additives are

Table. Quantum Yields for Photoisomerization $\text{1d} \rightarrow \text{2d}$.

[3]	Solvent	Additive (M)	ϕ^a
0.08	cyclohexane	----	0.010
0.09	diglyme	----	0.013
0.10	benzene	----	0.013
0.03	n-propyl bromide	----	0.013
0.08	benzene	cyclooctatetraene (0.11)	0.014
0.10	benzene	diene ^b (0.02-0.08)	0.012
0.10	benzene	fluorenone (0.9) (53) ^c	<0.003 ^d
0.09	benzene	benzophenone (1.0) (69) ^c	<0.003 ^d
0.007	benzene	valerophenone (0.4) (72) ^c	<0.003 ^d

^aRayonet reactor (325 - 385 nm), $30 \pm 1^\circ\text{C}$, valerophenone actinometer, estimated error $\pm 15\%$. ^b2,4-dimethyl-2,5-hexadiene ($E_T < 58 \text{ kcal/mol}$).

^cSensitizer E_T , kcal/mol. ^dUpper limit corrected for azepine absorption.

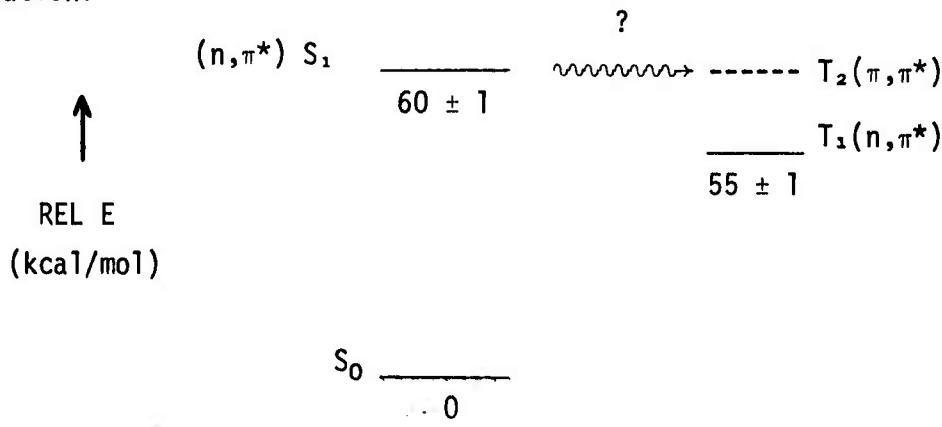
shown in the Table. The lack of quenching by diene and cyclooctatetraene (for which a very low triplet energy has been calculated³), along with the lack of sensitization in experiments where sensitizers absorbed $>75\%$ of the light, implicate a singlet excited state for valence isomerization of 1d .

That a triplet state of 1d is available was inferred from its quenching behavior. Conventional Stern-Volmer analysis of the quenching of valerophenone photoelimination⁴ and biacetyl phosphorescence in benzene as a function of $[\text{1d}]$ gave $k_q \tau = 56 \pm 8$ and $2.5 \pm 0.3 \times 10^5 \text{ M}^{-1}$, respectively. Using triplet lifetimes of valerophenone ($8.0 \times 10^{-9} \text{ sec}$)⁴ and biacetyl ($4.6 \times 10^{-4} \text{ sec}$)⁵, quenching constants are calculated ($k_q = 7.0 \times 10^9$ and $5.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, respectively).

Photolysis of 1d in benzene near its onset of absorption using an argon ion laser (457.9 nm) gave 2d with a quantum yield of 0.013 ± 0.004 (ferrioxalate

actinometry). Luminescence of I_d was not observed in benzene at room temperature or in an EPA glass at 77°K.

The reactivity of S_1 and the unreactivity of T_1 for I_d complete an excited state structure - reactivity pattern already in evidence for $\text{I}_a^{1a,b}$ and I_b^{1e} . The data further allow the relative location of states for I_d on the basis of the following (1) the effectiveness of laser emission (61 kcal/Einstein) at a wavelength which must be near the 0-0 transition (2) the quenching of valero-phenone photoelimination at near the diffusion controlled rate,⁶ (requiring $E_T(\text{I}_d) < 70$ kcal/mol); and (3) the quenching of biacetyl ($E_T = 55 - 56$ kcal/mol) phosphorescence at a rate short of the diffusion limit.⁶ The following Jablon-ski diagram is consistent with the data for I_d and respects a reasonable n, π^* S - T separation.



Importantly, a very low lying triplet ($E_T < 50$ kcal/mol), either of a planar, "resonance" stabilized 8e variety, as suggested for 4N cyclic hydrocarbon pi systems,³ or similar to I_a ($E_T = 47$ kcal/mol^{1b}) does not obtain for I_d . However, a π, π^* triplet at 60 kcal/mol or less seems likely if I_d be diene-like.⁷ This raises the possibility of an intrinsically rapid⁸ intersystem crossing to an unreactive triplet manifold which would account in part for the low isomerization quantum yield and the lack of quenching by a heavy atom solvent (n-PrBr).

Triplet counting experiments did not confirm the efficient formation of a reasonably

long lived triplet. Thus, $\tilde{1d}$ was no more than 1/10 as efficient in sensitizing the dimerization of 1,3-cyclohexadiene ($E_T = 51 - 52 \text{ kcal/mol}^7$) compared with benzophenone under parallel irradiation conditions. Intersystem crossing remains a possibility however, if the resulting triplet be very short lived or if energy transfer be insufficiently exothermic.⁶

The assignment and location of states for $\tilde{1d}$ provide important reference points for the heterocyclic trienes generally. In addition, the indirect photochemical and photophysical methods employed here may be extendable to such systems with somewhat unusual chromophores where detection of luminescence may be impossible.

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